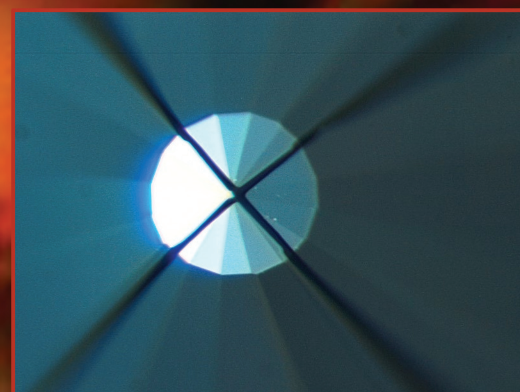
Putting the Squeeze on Materials



A new type of diamond anvil cell encapsulates tiny wires in a thin diamond film to reveal information about materials' behavior under high pressure.

FEW gemstones are as mesmerizing as diamonds. Livermore physicists also find diamonds attractive but for reasons other than their beauty. The researchers use flawless, polished diamonds in opposing pairs, or anvils, to slowly compress samples of materials at extreme pressures. This device, called a diamond anvil cell (DAC), forces materials to reveal new information about how their structure and electrical and magnetic properties change—sometimes drastically—in response to increasing pressure.

A DAC is a small mechanical press that forces together the small, flat tips (called culets) of two brilliant-cut diamond anvils. The diamond tips press on a microgram sample of a material, held within a metal gasket, to create extremely high pressures. Diamonds are used because they are the hardest known solid and so can withstand ultrahigh pressures. They also permit diagnostic radiation, such as x rays and visible light, to pass unhampered through their crystalline structure.

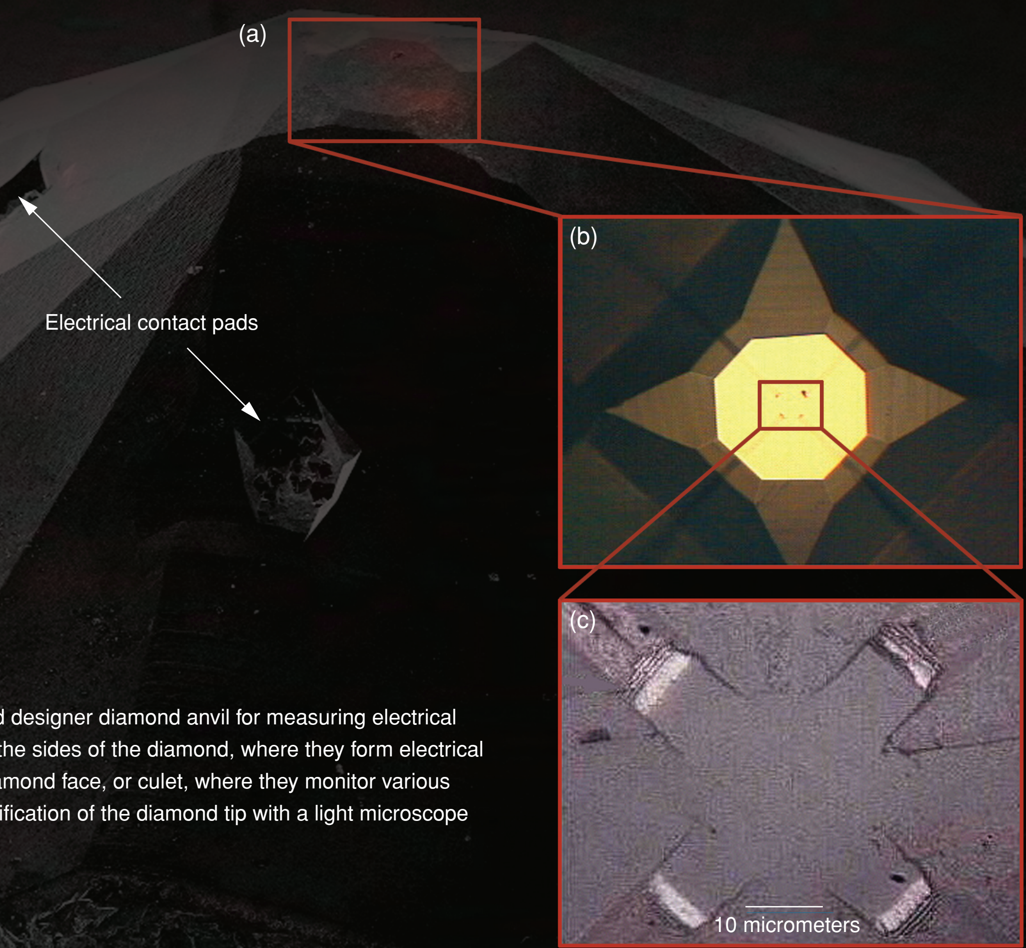
However, DAC studies of such properties as electrical conductivity and magnetic susceptibility are extremely difficult to perform. The 1-microgram samples have a diameter of about 75 micrometers, and diagnostic instruments cannot be placed close enough to them to make the required measurements. Problems especially arise when researchers try to obtain information about materials at static pressures above 1 million atmospheres, or 100 gigapascals (GPa). (For comparison, the atmospheric pressure at sea level is about 1/10,000th of 1 GPa, and the pressure at the center of Earth is about 3.6 million atmospheres.)

To overcome the problems posed by standard diamond anvils, Livermore researchers have taken advantage of recent improvements in diamond synthesis technology to fabricate microcircuits within the diamond anvils themselves. The tungsten microcircuits serve as tiny diagnostic instruments that measure data about materials' fundamental physical and mechanical properties under high pressures. The researchers call this modified tool a designer diamond anvil because the microcircuits can be altered to suit the needs of the experimenter.

Pressuring Materials to Change

Materials behave quite differently under extreme pressures than they do at normal atmospheric pressure. Oxygen, for example, becomes a shiny metal under ultrahigh pressure. In support of the National Nuclear Security Administration's Stockpile Stewardship Program, Livermore researchers are particularly interested in better understanding how nuclear weapon materials, such as plutonium and uranium, behave under high pressures.

Experiments with DACs provide stockpile stewardship data that complement data from shock experiments and tests driven by high explosives. All of these data improve the precision of computer codes that scientists use to model weapon performance and thus, help to ensure the safety and



Scanning electron micrographs show a completed designer diamond anvil for measuring electrical conductivity. (a) Tungsten microcircuits lead from the sides of the diamond, where they form electrical contact pads with instruments, to the tip of the diamond face, or culet, where they monitor various properties of the sample. (b, c) Progressive magnification of the diamond tip with a light microscope shows the termination of the tungsten wires.

reliability of the nation's aging nuclear weapons stockpile. In particular, experimental data are used to refine a material's pressure–volume–temperature relationship (its equation of state, or EOS) and the resulting structural changes (its phase diagram).

With DACs, researchers can measure material properties directly under static pressure, and they can vary pressures and temperatures slowly over the course of many hours. Livermore scientists are using designer DACs to learn how high pressures cause materials to change their magnetic properties, switch from insulators to metals, and alter their molecular structures.

"It is difficult to learn about electrical conductivity and magnetic properties with standard diamond anvils at high pressures," says Livermore physicist and designer anvil inventor Sam Weir. "Until recently, we were limited to trying to maneuver wires into place with tweezers, but these wires deform, break, and short-circuit. Our approach now is to build tiny tungsten wires inside the diamonds so they survive the high pressures. We lithographically fabricate thin-film wires on top of the anvil and then 'grow' a layer of diamond on top of the wires to protect them."

Designer Diamonds Hand-Fashioned

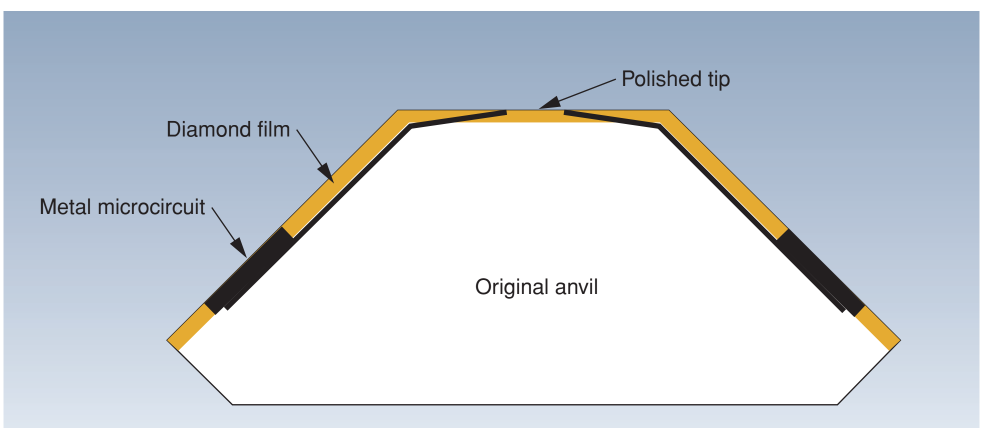
Every designer diamond anvil is custom-fabricated by researchers from Livermore and the University of Alabama at Birmingham. (See the box on p. 8.) The production team makes three types of designer diamond anvils: one for high-pressure electrical conductivity experiments, another for magnetic susceptibility experiments, and a third for electrically heating high-pressure samples to high temperatures. Each type features a unique pattern of microcircuits, usually made of tungsten, which are fabricated on the diamond tip and then encapsulated within a diamond film. These microcircuits terminate on the diamond's sides, where they can be connected to instruments that collect data with high accuracy and sensitivity.

Electrical conductivity experiments use four to eight tungsten wires, magnetic susceptibility experiments require a microloop of about ten turns of wire, and high-temperature experiments use eight wires.

The designer diamond anvil is placed in a beryllium–copper cell about 6 centimeters tall and 3 centimeters in diameter. The cell, in turn, is placed in a small device consisting of a gear-driven piston and cylinder mechanism that can push diamond tips together with a controlled force great enough to generate ultrahigh pressures between the tips. Turning the knob on this mechanism pushes the designer diamond anvil (usually located on the bottom) against a stationary, standard diamond anvil, increasing the pressure and maintaining it indefinitely.

Because diamonds are transparent, scientists can use DACs to make optical and x-ray measurements. Livermore researchers use a light microscope to monitor an experiment. In addition, they place a tiny chip of ruby next to the sample to measure pressure. When green or blue visible laser light shines on the ruby, the ruby emits red light at a wavelength of about 694 nanometers. As the pressure increases, the wavelength increases.

For some experiments, the researchers transport the DAC to a source of very bright, highly collimated x rays, such as the National Synchrotron Light Source at Brookhaven National Laboratory in New York. The scientists pass a beam of x rays through the sample and both diamonds and record the resulting diffraction pattern on an x-ray film or detector. Changes in the diffraction pattern reveal how a material's structure responds to pressure.



A designer diamond anvil uses a one-third-carat diamond. Tungsten metal microcircuits are fabricated on the diamond's 300-micrometer-wide polished tip. These microcircuits are covered with a thin film of diamond and then polished to reveal the tips of the microcircuits on the top of the diamond face.

Focus on Two Element Groups

Many designer DAC experiments focus on two groups of elements—the lanthanides and the actinides—which include the nuclear weapon metals uranium and plutonium. The experiments provide data about lanthanides and actinides that standard DAC techniques and dynamic experiments cannot supply.

Most of the pressure-driven changes the researchers see can be explained by the behavior of a material's electrons. Weir explains that under extreme pressures, certain electrons, which are normally tightly held within an atom's inner electron bands or shells, can move about, resulting in changes in material properties and molecular structures. In lanthanides and actinides, these electrons belong to an atom's 4f and 5f bands. "Most experiments don't give insight about the cause of volume changes," says Weir. "Our experiments do because we can explain the changes by the delocalization of electrons from specific bands they normally occupy."

How Insulators Become Metals

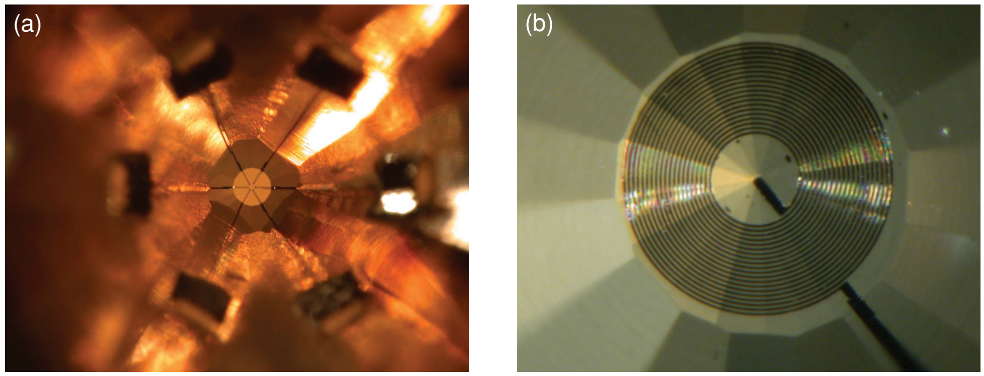
Postdoctoral researcher Reed Patterson performed one of the first experiments with a designer DAC to determine why compounds such as manganese oxide (MnO) are insulators—that is, why they resist the movement of electrons. Electrical conductivity experiments, which probe materials' insulating nature, can only be accomplished at ultrahigh pressures using DACs equipped with designer diamond anvils.

Patterson performed several high-pressure electrical conductivity experiments on a MnO sample. The experiments used a designer diamond anvil with eight tungsten probes measuring 10 micrometers wide and 0.5 micrometer thick. The probes were covered with diamond film and exposed only at the surface near the center of the diamond anvil's culet, where they make contact with the MnO sample.

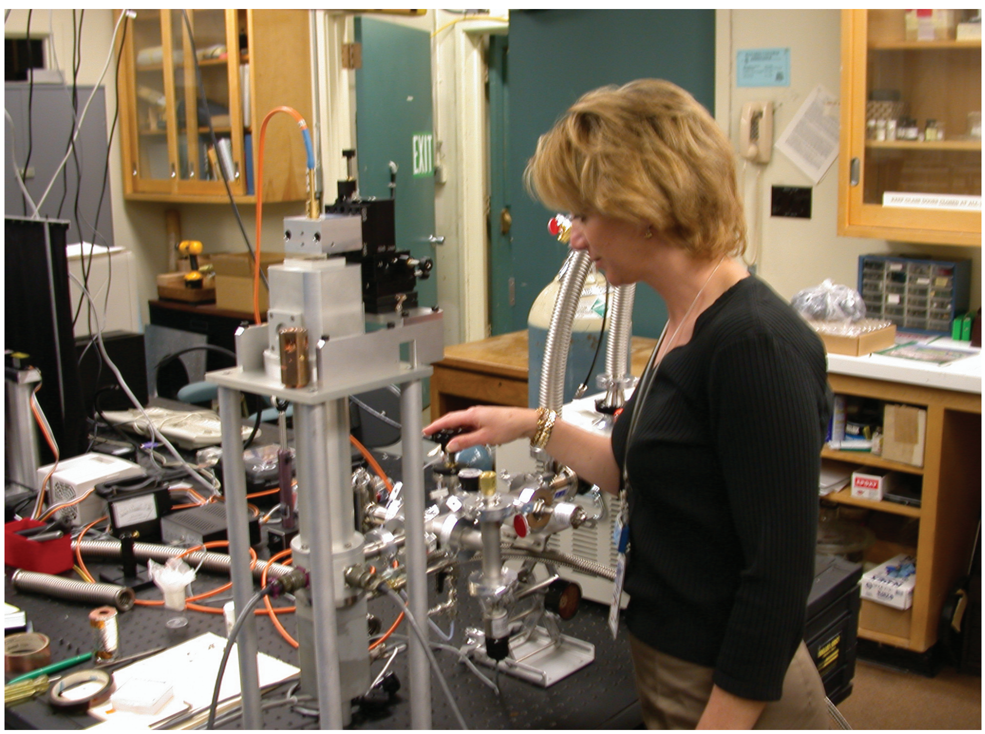
Electrical conductivity was determined by passing a direct current through the wires to the sample and measuring the electrical resistance as a function of pressure. The researchers noted that the sample's electrical resistance rapidly decreased by a factor of 100,000 between 85 and 106 GPa, signaling the transformation of MnO from an insulator to a metal.

The observations provide strong evidence for a pressure-induced insulator-to-metal transition beginning at about 90 GPa, says Weir. "When we squeeze a material, its atoms are forced into a different orientation, which causes the delocalization of electrons. Manganese oxide becomes a metal under these conditions because certain electrons are free to flow instead of staying localized with one atom." The transition is also marked by a nearly 10-percent reduction in the sample's volume, as the crystalline lattice shifts to accommodate the new electronic configuration.

Weir says the results shed light on the high-pressure behavior of other elements with bound electrons, such as lanthanides



Each type of designer diamond anvil features a unique pattern of microcircuits that are fabricated on the diamond tip. A light microscope shows the tip for (a) an electrical conductivity experiment and (b) a magnetic susceptibility experiment.



Livermore scientist Chantel Aracne monitors a high-pressure experiment using a designer diamond anvil cell.

and heavy actinides. Livermore experiments on the lanthanide praseodymium showed that a previously reported 10-percent volume collapse at about 20 GPa coincides with a sudden 60-percent decrease in the metal's resistivity. The sudden drop in resistivity indicates that praseodymium's bound f electrons become delocalized at this pressure. A similar 10-percent volume decrease has been reported in high-pressure experiments on the lanthanide gadolinium at 60 GPa. High-pressure resistivity experiments are under way to investigate whether gadolinium's bound f electrons become delocalized at this pressure.

The researchers are also examining the electrical conductivity of depleted uranium (uranium left over from uranium enrichment processes) at high pressure. They have not discovered significant changes in resistivity that might indicate a change in its electronic or crystallographic structure.

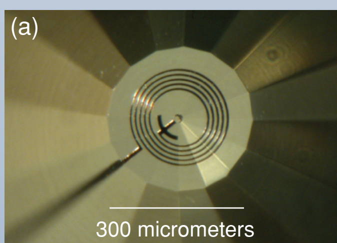
Probing Magnetic Susceptibility

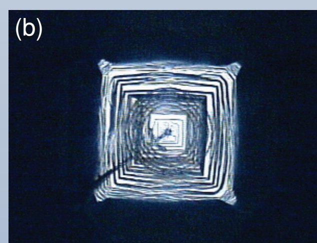
In a project funded by the Laboratory Directed Research and Development (LDRD) Program, Livermore physicists have developed a new type of designer diamond anvil that is equipped with tiny magnetic sensing coils. They are using these

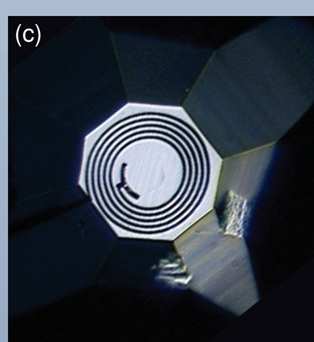
Building a Designer Diamond Anvil

Fabricating a designer diamond anvil is a multistep process that begins with a brilliant-cut, one-third-carat diamond. The diamond's tip must be free of inclusions or defects that could weaken the diamond when it is placed under pressures equivalent to several million times Earth's atmospheric pressure at sea level. At pressures of 100 gigapascals (GPa) and above, the diamonds occasionally shatter into dust. However, at more moderate pressures, they can be reused many times.

The tip of the designer diamond is polished until a flat surface, called a culet, is formed, providing a surface on which the sample can be placed. For experiments at pressures below 50 GPa, the diamond culet ranges from 100 to 500 micrometers in diameter. For experiments above 50 GPa, the culet is beveled downward at the sides so the tip remains relatively flat in response to the pressures.







A designer diamond anvil is made by (a) lithographically fabricating tungsten microcircuits on the diamond's flattened tip, (b) depositing a thin film of diamond over the microcircuits, and (c) polishing the diamond tip so that only the ends of the microcircuits are exposed. This particular designer diamond anvil measures magnetic susceptibility.

Metal microcircuits, or microprobes, made of tungsten are patterned on the tip. Two-dimensional optical lithography, a process used in the semiconductor industry, creates these patterns on the culet. Livermore's three-dimensional laser pantography system, which is managed by Vincent Malba in the Engineering Directorate, is then used to continue the lines on the steep walls of the anvil. Next, a sputtering chamber is used to deposit a thin film of tungsten ions onto the lines of photoresist. Typical probe line widths measure 10 to 30 micrometers. These line patterns extend down the side of the diamond anvil to 125-micrometer-square metal connection points, where leads from external instruments can be connected.

After the tungsten microcircuits are fabricated, a single crystal layer of diamond is deposited on the anvil using a gaseous mixture of 2 percent methane and 98 percent hydrogen. The diamond layer is applied through microwave plasma chemical vapor deposition, a process developed by Vogesh Vohra and Paul Baker at the University of Alabama at Birmingham.

This process lays down a thin film of diamond that varies in thickness from 10 micrometers on the culet to 50 micrometers down the anvil sides. The film is applied at an average rate of 10 micrometers per hour. The film's crystallographic orientation exactly matches that of the substrate. This so-called epitaxial diamond encapsulation is crucial to ensuring that the microprobes survive high pressures.

The rough diamond surface on the anvil's culet is polished to a smooth finish with a tolerance of about 1 micrometer, leaving the microprobes completely encapsulated in diamond except at the tip on the culet and the exposed electrical connectors at the end of the wires on the diamond anvil's sides. These pads make contact with the leads from diagnostic instruments.

Researchers place a 250-micrometer-thick metal gasket on top of the culet. Then they drill a 30- to 150-micrometer-diameter hole in the center of the gasket and place the sample in it. Because diamonds are small, material samples must be the size of pinheads—about 75 micrometers wide. For some experiments, a liquid, gas, or solid is added to the sample to help distribute the compressive force of the diamond faces.

new designer diamond anvils to study the magnetic susceptibility of lanthanides and actinides—that is, how they respond to strong magnetic fields while being subjected to extreme pressures. Data from magnetic susceptibility experiments are expected to improve scientists' understanding of electronic properties and, hence, the different phases of uranium and plutonium.

In the presence of a magnetic field, electrons may align themselves in various ways, much like microscopic bar magnets, or they may not respond at all. Each response reflects the subtle and often competing electron–electron interactions at play in many materials. "Our current understanding of magnetism and magnetic order is far from complete because of electron–electron interactions," says Livermore physicist Damon Jackson, who is leading the experiments.

Magnetic susceptibility experiments with standard DACs are challenging because of the sample's minuscule size and the limitations of sensing coils when they cannot be placed extremely close to the sample. As a result, poor measurement sensitivity and low signal-to-background-noise ratios are common. Designer diamond anvils fabricated for magnetic susceptibility experiments, however, significantly increase data quality because the sensing coils can be placed within a few micrometers of the high-pressure sample.

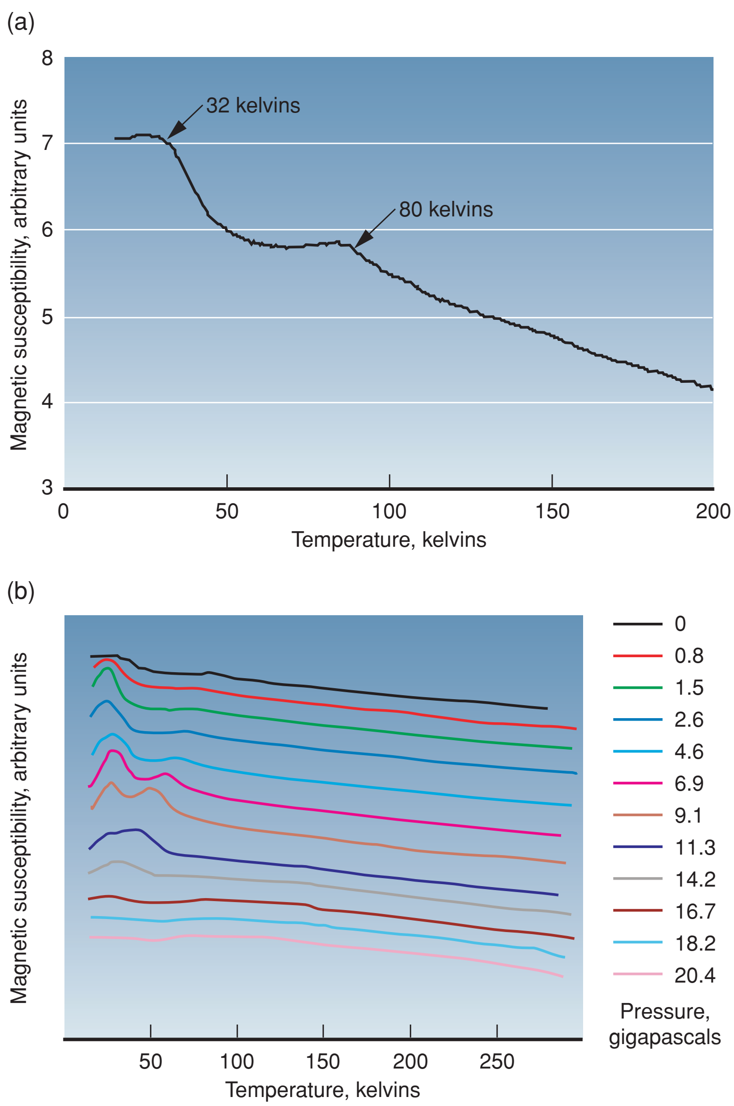
In these experiments, an excitation coil surrounding the sample creates a varying magnetic field. The sample's response is then measured by detecting the voltage induced in a sensing coil embedded in the tip of a designer diamond anvil. Any changes in the magnetic susceptibility of the sample alter the amount of magnetic flux passing through the sensing coil, which results in a change in voltage.

The diamond-encapsulated sensing coil is located just 10 to 20 micrometers below the sample, to increase the sensitivity of the diagnostics. The microcoil typically uses between 10 and 20 turns of tungsten wire (a 20-turn microcoil measures 280 micrometers in outer diameter with a 2.5-micrometer line width). Experiments demonstrated that the microcoils' intrinsic signal-to-background-noise ratio is about 10,000 times higher than with old-style DACs, in which sensing coils are located much farther from the sample.

The excitation coil consists of about 55 turns of copper wire and is wrapped around a standard diamond anvil. The sample, measuring about 75 micrometers in diameter and 50 micrometers thick, is contained within a hole drilled into a metal gasket and sandwiched between the diamond anvils. Typical excitation currents are 10 to 90 milliamperes, which yield magnetic fields up to about 6 gauss. The researchers cool the sample with a helium cryostat to collect magnetic susceptibility data as a function of temperature.

Probing Magnetic Effects

Magnetic susceptibility is a useful probe of f-electron behavior in lanthanides and actinides because the magnetism exhibited in these metals is usually due to their f electrons. High pressures compress the atomic lattice and, thereby, alter the



Experiments with the designer diamond anvil to measure magnetic susceptibility showed two transition states for erbium at room pressure. (a) Erbium's magnetic order is random at room termperature. When it is cooled to 80 kelvins, the magnetic order of its electrons alternates atom by atom. When cooled to 32 kelvins, the electrons from every atom are aligned. (b) Under high pressures, both of erbium's transition temperatures shift in response to the reduced distances between atoms.

magnetic states of the f electrons. Thus, high-pressure magnetic susceptibility experiments provide important physical insights into the electronic interactions affecting the f electrons and, ultimately, the high-pressure EOS of these metals.

When erbium was tested at room pressure, experiments showed two transition states. (See the figure on p. 9.) At room temperature, erbium's magnetic order is random. When it is cooled to 80 kelvins, its electrons become antiferromagnetic; that is, f electrons in alternate atoms show opposite magnetic order. When cooled to 32 kelvins, the sample becomes ferromagnetic, in which all f electrons from every atom are aligned. Under high pressures, both transition temperatures shift in response to changes in the reduced distances between atoms.

Livermore scientists have also conducted magnetic susceptibility experiments on the lanthanides terbium, dysprosium, holmium, and thulium. All show similar magnetic properties in response to temperature and pressure changes.

"We now have an apparatus that can perform highly sensitive magnetic susceptibility experiments on uranium and plutonium samples at extreme pressures," says Jackson. He plans to start experiments on plutonium to characterize its magnetic behavior over a wide range of pressures and temperatures.

Experiments Heat Up

Weir and Jackson recently developed a prototype for yet another type of designer diamond anvil, which uses ohmic heating for experiments at high temperatures and high pressures. This type of designer diamond anvil delivers relatively large amounts of electrical current to the sample and heats it, much like a tiny heating pad would, but to temperatures of thousands of degrees. Six microprobes deliver current for heating, and another two measure the sample's electrical resistance. Sharp changes in resistance indicate phase changes.

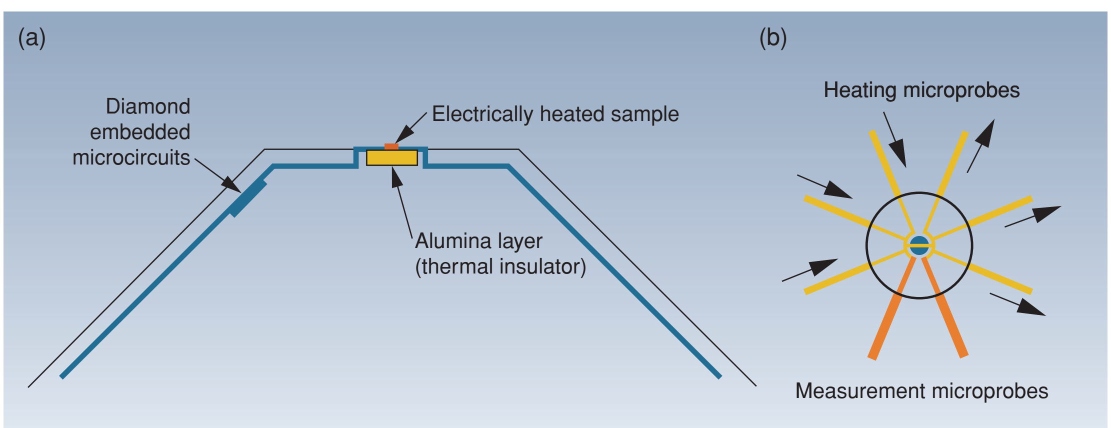
In designing this new type of designer diamond anvil, the physicists had several special requirements to consider. For example, diamond at room temperature has a high thermal conductivity. As a result, using ohmic heating to directly heat a sample to a high temperature is difficult because much of the heat is immediately transferred from the sample to the diamond. To eliminate this problem, the researchers embed the sample in a layer of powdered aluminum oxide (alumina). Using optical lithography and oxygen plasma etching, they excavate a small pit on the culet. The pit, which is 25 micrometers in diameter and about 25 micrometers deep, is packed full of alumina powder, and a sample is placed inside it. As microprobes heat the sample, the alumina-filled pit provides an insulating environment, allowing the sample to withstand significant deformation even at ultrahigh pressures.

Heating experiments on tungsten samples have achieved a maximum of 2,900 kelvins, but adds Weir, "Our heating experiments are just in their infancy."

Looking to the Future

As physicists gain experience in using designer diamond anvils, they are focusing on understanding plutonium under high pressure. In a project funded by LDRD, the researchers are looking for a phase transformation in plutonium at close to 0 kelvin, or absolute zero, the point at which all molecular motion ceases. This phase transformation is called a quantum critical point because near absolute zero, quantum mechanics fluctuations are important and heat fluctuations are not.

Quantum critical points often have important effects at much higher temperatures and could help explain aspects of plutonium's puzzling behavior.



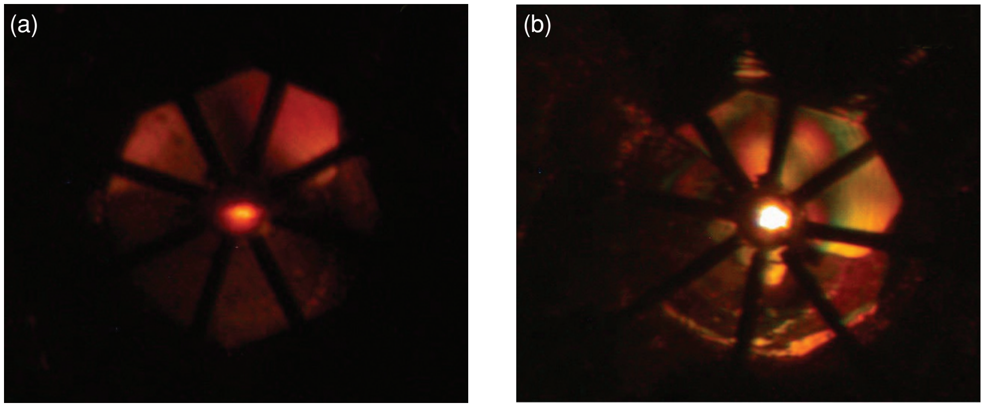
An ohmic-heating designer diamond anvil is used for experiments at high temperatures and high pressures: (a) side view and (b) top view. In this device, six microprobes work to electrically heat the sample, and two microprobes measure its electrical resistance. Because diamond at room temperature has a high thermal conductivity, researchers embed the sample in a layer of powdered aluminum oxide (alumina), which acts as a thermal insulator.

"Plutonium has many structural transitions or phases, which might be the result of a quantum critical point that exists only near 0 kelvin," says Jackson.

Quantum critical points are typically investigated by cooling a material to the lowest practical temperature and then varying a material property, such as chemical composition, or applying a high pressure or a magnetic field. The LDRD project is examining how plutonium behaves in response to changes in temperature, magnetic field, and pressure.

Ohmic-heating experiments to be conducted at Brookhaven are also being planned. "We want to take images of the compression of plutonium's lattice as we elevate pressure and temperature," says Weir. He foresees using two designer diamond anvils in combination for the first time to conduct the plutonium heating experiments: one to heat the sample and another to measure its magnetic susceptibility.

Finally, Weir and Jackson are preparing to begin an ambitious project to use a diamond anvil cell to compress solid hydrogen to more than 300 GPa and study its conductive properties. Livermore researchers were the first to metallize high-temperature fluid hydrogen by using a shock compression technique to squeeze hydrogen to ultrahigh densities. The upcoming effort, funded by LDRD, will attempt to metallize hydrogen at low temperatures, where it is in its solid form. Some scientists consider the search for metallic solid hydrogen to be the Holy Grail of high-pressure physics research.



In heating experiments of tungsten, temperature was increased from (a) 1,200 kelvins to (b) a maximum of 2,900 kelvins, creating a glow in the ultrahot, high-pressure (50-gigapascal) sample.

Ultradense hydrogen has long been the subject of intense experimental and theoretical research because of its fascinating properties. Jackson explains that as the lightest element, hydrogen has large quantum fluctuations, even at 0 kelvin, making it difficult for theorists to accurately predict its properties. Hydrogen's properties have important implications for planetary physics because the interiors of the giant planets Jupiter and Saturn are believed to have cores of dense, metallic hydrogen. Ultradense hydrogen also is of interest to stockpile stewardship. Multiple-shock compression experiments on hydrogen to the metallic state have accelerated the development of new hydrogen EOS models, which are important in studies of inertial confinement fusion and other applications.

William Evans and Choong-Shik Yoo from Livermore's Physics and Advanced Technologies Directorate will join Jackson and Weir in the research project. "This ambitious effort will require pushing designer diamond anvils to new extremes in pressure," says Weir. "But if we're successful, it will result in a significant scientific breakthrough."

The future looks bright for designer DACs. Diamonds may well become a physicist's best friend.

—Arnie Heller

Key Words: actinides, designer diamond anvil, diamond anvil cell (DAC), electrical conductivity, ultradense hydrogen, Laboratory Directed Research and Development (LDRD) Program, lanthanides, laser pantography, magnetic susceptibility, microcircuits, plutonium, uranium.

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